

Structure of compound I ( $\text{MgPc}(3,5\text{-lut})_2$ ) is built of MgPc moieties axially coordinated with two ligand molecules (4+2 type). These fragments are stacked together with  $\pi$ - $\pi$  interactions to form layered structure. Mg atom lies in the plane of four N isoindole atoms of Pc aromatic ring, it occupies the special position lying in the center of inversion.

Contrary to compound I, compounds II, III and IV are characterized by 4+1 type of Mg metal center coordination site. Water molecule is introduced in closest coordination sphere of Mg atom, replacing the lutidine molecules from Mg environment. Compound II is characterized by the hydrogen bond between one of water molecule H atoms and lutidine N aromatic ring atom as an acceptor. Another H atom of coordinated water molecules form hydrogen bond with the azamethine N atom of the adjacent MgPc molecule, so that the chains going in the *a* axis direction are formed. 3,5-Lutidine molecules are  $\pi$ - $\pi$  stacked between the neighboring MgPc moieties. The characteristic feature of this compound is the absence of back-to-back type dimers in its structure. Up-to-date all of MgPc coordination compounds with 4+1 type Mg atom environment possessed this kind of dimers.

Compounds III and IV are built of  $\text{MgPc}(\text{H}_2\text{O})$  moieties and two lutidine molecules hydrogen bonded with them. These  $\text{MgPc}(\text{H}_2\text{O})\cdot 2\text{L}$  moieties are stacked in the structure to form back-to-back type dimers. The deviation of Mg atom from the mean plane of four isoindole N atoms is equal to 0.553(2), 0.510(1) and, 0.464(1) Å, respectively for II, III and IV. Saucer-shaped geometry of MgPc molecule is flattered by the back-to-back type dimers formation in the case of compounds III and IV. The highest Mg atom off-plane deviation value in the compound II correlates well with the absence of back-to-back type dimers.

The tendency to form 4+2 type coordination compounds with N-donor ligands and 4+1 – with O-donor ones is observed.

**Keywords:** macrocyclic ligands; coordination compounds; phthalocyanines

#### FA4-MS06-P08

**Spectroscopic and Crystallographic Characterization of Bis(azido) Cobalt(III) Porphyrinates.** Bader Bel Haj Ali<sup>a</sup>, Mohamed Salah Belkhiria<sup>a</sup>, Michel Giorgi<sup>b</sup>, Habib Nasri<sup>a</sup>. <sup>a</sup>Laboratoire de Physico-chimie des matériaux, Faculté des Sciences de Monastir, Avenue de l'environnement, 5019 Monastir, Tunisia. <sup>b</sup>Spectropole, Faculté des Sciences de St-Jérôme, Université d'Aix-Marseille, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France.

E-mail : [belhaj\\_bader@yahoo.fr](mailto:belhaj_bader@yahoo.fr)

While iron porphyrins are frequently used as synthetic model systems, cobalt(III) porphyrins exhibit catalase-like activity in the disproportionation of  $\text{H}_2\text{O}_2$ . Here we present the results of our investigation on new hexacoordinate

bis(azido) cobalt(III) porphyrinates with picket fence porphyrin (TpivPP) and the octaethylporphyrin (OEP). The two derivatives were characterized by UV-vis. IR and <sup>1</sup>H NMR spectroscopies. Both complex ions  $[\text{Co}^{\text{III}}(\text{TpivPP})(\text{N}_3)_2]^-$  (**I**) and  $[\text{Co}^{\text{III}}(\text{OEP})(\text{N}_3)_2]^-$  (**II**) crystallize in the monoclinic space group P2<sub>1</sub>/n.

(**I**): Z = 4, a = 12.9596(2) Å, b = 27.5833(5) Å, c = 23.8539(5) Å,  $\beta$  = 105.134(1)°, at 293 K.  $R_1$  = 0.0942,  $wR_2$  = 0.2489 for 10119 observed reflections [ $I \geq 2\sigma(I)$ ].

(**II**): Z = 4, a = 115.3589(2) Å, b = 17.9122(3) Å, c = 21.276053 Å,  $\beta$  = 101.370(1)°, at 293 K.  $R_1$  = 0.0759,  $wR_2$  = 0.2736 for 12646 observed reflections [ $I \geq 2\sigma(I)$ ].

The average equatorial Fe–Np distance value for the TpivPP derivative which is 1.962(4) Å is quit shorter than the one of the OEP bis(azido) species (Co–Np = 1.984(3) Å). The average value of the Co–N(azido) distance of (**I**) is 1.945(6) Å is shorter than the Co–N(azido) bond length of derivative (**II**) (1.977(3) Å). Both cobalt(III)-azido distances in compounds (**I**) and (**II**) are significantly shorter than the iron(II) monoazido species  $[\text{Fe}^{\text{II}}(\text{TpivPP})(\text{N}_3)]^-$  [1]. This indicates that the Co<sup>III</sup>–N(azido) distance is stronger than the Fe<sup>II</sup>–N(azido) bond length in metalloporphyrins.

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#### FA4-MS06-P09

**Extrusion/Uptake of Alcohols by Silver Carboxylate Coordination Networks.** Inigo Vitorica Yrezabal<sup>a</sup>, Harry Adams<sup>a</sup>, Lee Brammer<sup>a</sup>. <sup>a</sup>Department of Chemistry, University of Sheffield. Email: [Chp08iv@sheffield.ac.uk](mailto:Chp08iv@sheffield.ac.uk)

Chemical reactions in the organic solid state are uncommon but well-established. They involve the formation of covalent bonds between neighbouring moieties as a result of photochemical or thermal activation [1]. In this work a class of single crystal-single crystal reactions within nonporous crystals of a coordination network will be presented, wherein bonds are broken and formed in a ligand substitution reaction at silver (I) centre. It has been shown that the behaviour of the Ag<sup>+</sup> ions in these networks show structural similarities to the hydrogen “ions” in the carboxylic acid structures [2]. We have extended this equivalence by inclusion of an alcohol molecule in the  $[\text{Ag}_2(\text{O}_2\text{CR})_2]$  dimer [3]. A series of compounds of general formula  $[\text{Ag}_4(\text{TMP})_3(\text{O}_2\text{CR})_4(\text{ROH})_2]$  (TMP=2,3,5,6-tetramethylpyridine, R<sub>f</sub>=perfluoroalkyl group, ROH=alcohol) have been prepared and crystallographically characterised. The release of the alcohol molecules from the expanded dimer and their extrusion from the crystals of the coordination network material  $[\text{Ag}_4(\text{TMP})_3(\text{O}_2\text{CR})_4(\text{ROH})_2]$  yielding the alcohol-free network  $[\text{Ag}_4(\text{TMP})_3(\text{O}_2\text{CR})_4]$  has been investigated. Both this process and the reverse reaction involving different alcohol uptake occur in single-crystal-single crystal reactions.

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**Keywords:** silver perfluorocarboxylates; alcohol; single-crystal-to-single-crystal reaction

#### FA4-MS06-P10

### Synthesis and Structural Characterization of New Heteroleptic Aluminium Alkoxides and Siloxides.

Sergio Pedrosa<sup>a</sup>, Marta E.G. Mosquera<sup>a</sup>, Pilar Gómez-Sal<sup>a</sup>. <sup>a</sup>*Departamento de Química Inorgánica. Universidad de Alcalá, Campus Universitario, Alcalá de Henares, 28805-Madrid, Spain.*

E-mail: [sergio.pedrosa@uah.es](mailto:sergio.pedrosa@uah.es)

Aluminium attracts wide attention not only because of its rich chemistry, but also due to the important applications that exhibit in areas as diverse as organic synthesis, electronic materials, structural materials and catalysis.[1] In particular, aluminoxanes play a key role as co-catalysts in the Ziegler-Natta polymerization processes.[2] As well, aluminium alkoxide derivatives have proven to be very efficient catalysts in many polymerization reactions, such as ring opening polymerization.[3]

As a continuation of our work on functionalized aryloxide aluminium derivatives[4] we have extended our studies to silanols. The generation of molecular aluminosiloxanes compounds has an additional interest since this kind of species have shown to be useful both as model compounds for open-framework silicates and as precursors for the preparation of mixed metal oxide materials under mild conditions.[5]

We are particularly interested in achieving a good control of the structures obtained by controlling the reactions conditions. In this communication we present our latest results and our studies in relation to the different outcome depending on the aluminium precursor. Thus when  $\text{AlMe}_3$  is used the expected dimer  $[\text{AlMe}_2(\text{OR})_2]_2$  is formed, however if  $\text{AlClMe}_2$  is the precursor, unexpected results are attained such as the mixed alkoxide/syloxide derivative  $[\text{AlCl}(\text{OR})\text{OSi}(\text{OR})_3]_2$  shown in figure 1.

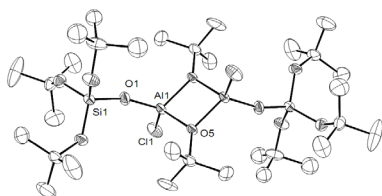


Figure1.

The new derivatives prepared were determined by X-ray diffraction methods, elemental analysis and NMR.

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**Keywords:** aluminum compounds; alkoxides; inorganic and organometallic compounds

#### FA4-MS06-P11

### Double Complex Salts with $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ Cation and $[\text{OsCl}_6]^{2-}$ Anion: Synthesis and Properties.

Crystal Structure of the  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2[\text{OsCl}_6]_2\text{Cl}_2$ .

Ilya Korolkov<sup>a</sup>, Svetlana Martynova<sup>a</sup>, Kirill Yusenkov<sup>b</sup>, Sergey Korenev<sup>a</sup>. <sup>a</sup>*Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia.* <sup>b</sup>*Inorganic Chemistry II - Organometallic and Materials, Ruhr-University Bochum, Germany.*

E-mail: [x-vizor@yandex.ru](mailto:x-vizor@yandex.ru)

Recently, interest in new energy sources and accumulators based on superfine metal catalysts deposited on the carbon supporter was grown [1, 2]. Ruthenium containing alloys show an extraordinary electrochemical activity and CO resistance [3]. This work continues a research of double complex salts, which are perfect precursors for obtaining solid solutions of platinum metals.  $[\text{Ru}(\text{NH}_3)_5\text{Cl}][\text{OsCl}_6]$  (**I**) was obtained by mixing of hot water solutions of  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $\text{Na}_2[\text{OsCl}_6]$ . The residue was washed with water and acetone, then dried in air. Yield is 85 - 90%. A synthesis of  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2[\text{OsCl}_6]_2\text{Cl}_2$  (**II**) was carried out with mixing of  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  powder,  $\text{Na}_2[\text{OsCl}_6]$  water solution and 0,1 M HCl. The mixture was left for 5 days in the dark place. The formed residue was washed with water and acetone, then dried in air. Yield is 85 - 90%. Cell parameters of **I** were refined by Rietveld method using  $[\text{Ru}(\text{NH}_3)_5\text{Cl}][\text{OsCl}_6]$  structure as a model [5]:  $a = 11,5931(4)$ ,  $b = 8,3181(3)$ ,  $c = 15,2344(4)$  Å;  $\beta = 90,707(4)^\circ$ ;  $V = 1469$  Å<sup>3</sup>; space group  $P2_1/m$ ;  $Z = 4$ . The crystal structure of **II** was determined with a X8APEX Bruker diffractometer (MoK $\alpha$ -radiation, graphite monochromator). Crystal structure data:  $C2/m$  space group,  $a = 11,1849(8)$  Å,  $b = 7,9528(6)$  Å,  $c = 13,4122(9)$  Å,  $V = 1175,75$  Å<sup>3</sup>,  $Z = 2$ . According to XRD data, **II** is isostructural to  $[\text{M}^I(\text{NH}_3)_5\text{Cl}]_2[\text{M}^{II}\text{Cl}_6]_2\text{Cl}_2$ , where  $\text{M}^I = \text{Rh, Ir, Co}$  and  $\text{M}^{II} = \text{Re, Os, Ir, Pt}$  [4]. Os-Cl bond lengths in the complex anion lay between 2,328-2,356 Å, Ru-N average bond length in complex cation is 2,111 Å, Ru-Cl is 2,334 Å. Distances between metals are typical for this kind of compounds. The smallest Ru...Os distance is 5,773 Å. Thermal stability of the complexes in different atmospheres was also investigated. It was found that the decomposition of **I** or **II** in hydrogen or helium atmosphere at 650° C gives a single-phase metal product with the hcp lattice. Cell parameters of obtained phases are close to cell parameters of original Ru-Os alloys obtained at 2000° C [6, 7].